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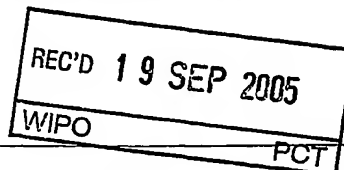
## PATENT COOPERATION TREATY



## PCT

## INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)



Applicant's or agent's file reference MDX,001-PCT	<b>FOR FURTHER ACTION</b> See Form PCT/PEA/416	
International application No. PCT/GB2004/001373	International filing date (day/month/year) 30.03.2004	Priority date (day/month/year) 31.03.2003
International Patent Classification (IPC) or national classification and IPC C23F11/16		
Applicant MIDDLESEX SILVER CO. LIMITED et al.		
<p>1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 8 sheets, including this cover sheet.</p> <p>3. This report is also accompanied by ANNEXES, comprising:</p> <p>a. <input checked="" type="checkbox"/> sent to the applicant and to the International Bureau) a total of sheets, as follows: (39)</p> <p><input checked="" type="checkbox"/> sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).</p> <p><input type="checkbox"/> sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.</p> <p>b. <input type="checkbox"/> (sent to the International Bureau only) a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).</p>		
<p>4. This report contains indications relating to the following items:</p> <p><input checked="" type="checkbox"/> Box No. I Basis of the opinion</p> <p><input type="checkbox"/> Box No. II Priority</p> <p><input type="checkbox"/> Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p><input type="checkbox"/> Box No. IV Lack of unity of invention</p> <p><input checked="" type="checkbox"/> Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p><input type="checkbox"/> Box No. VI Certain documents cited</p> <p><input type="checkbox"/> Box No. VII Certain defects in the international application</p> <p><input checked="" type="checkbox"/> Box No. VIII Certain observations on the international application</p>		
Date of submission of the demand  25.10.2004	Date of completion of this report  15.09.2005	
Name and mailing address of the international preliminary examining authority:   European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016	Authorized Officer  Handrea-Haller, M  Telephone No. +31 70 340-4823  	

**INTERNATIONAL PRELIMINARY REPORT  
ON PATENTABILITY**

International application No.  
PCT/GB2004/001373

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**Box No. I Basis of the report**

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1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.
- ☐ This report is based on translations from the original language into the following language , which is the language of a translation furnished for the purposes of:
- ☐ international search (under Rules 12.3 and 23.1(b))
  - ☐ publication of the international application (under Rule 12.4)
  - ☐ international preliminary examination (under Rules 55.2 and/or 55.3)
2. With regard to the **elements\*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report):*

**Description, Pages**

1-35 received on 13.07.2005 with letter of 13.07.2005

**Claims, Numbers**

1-23 received on 13.07.2005 with letter of 13.07.2005

- ☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing
3. ☐ The amendments have resulted in the cancellation of:
- ☐ the description, pages
  - ☐ the claims, Nos.
  - ☐ the drawings, sheets/figs
  - ☐ the sequence listing (*specify*):
  - ☐ any table(s) related to sequence listing (*specify*):
4. ☒ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
- ☒ the description, pages 9
  - ☒ the claims, Nos. 1,10, 22,23
  - ☐ the drawings, sheets/figs
  - ☐ the sequence listing (*specify*):
  - ☐ any table(s) related to sequence listing (*specify*):

\* If item 4 applies, some or all of these sheets may be marked "superseded."

**INTERNATIONAL PRELIMINARY REPORT  
ON PATENTABILITY**

International application No.  
PCT/GB2004/001373

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**Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

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**1. Statement**

Novelty (N)	Yes: Claims	1-23
	No: Claims	
Inventive step (IS)	Yes: Claims	7-14, 19-21
	No: Claims	1-6, 15-18, 22, 23
Industrial applicability (IA)	Yes: Claims	1-23
	No: Claims	

**2. Citations and explanations (Rule 70.7):**

**see separate sheet**

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**Box No. VIII Certain observations on the international application**

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The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

**see separate sheet**

**Re Item V**

**Reasoned statement with regard to novelty, inventive step or industrial applicability;  
citations and explanations supporting such statement**

1 The following documents are referred to in this communication:

D1: GB-A-1 130 540 (GODDARD & SONS LTD J) 16 October 1968 (1968-10-16)

D2: US-A-3 503 883 (COX BERNARD CARLTON ET AL) 31 March 1970 (1970-03-31)

D3: HAN S M ET AL: "FORMATION OF ALKANETHIOL MONOLAYER ON GE(111)"  
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, XX, XX, vol. 123, 2001,  
pages 2422-2425, XP001193899 WASHINGTON,US ISSN: 0002-7863

D4: GB-A-2 255 348 (METALEUROP RECH) 4 November 1992 (1992-11-04)

D5: WO 02/095082 A (JOHNS PETER GAMON) 28 November 2002 (2002-11-28)

**2 AMENDMENTS**

2.1 The amendments filed with the letter dated 13.07.2005 introduce subject-matter which extends beyond the content of the application as filed, contrary to Article 34(2)(b) PCT. The amendments concerned are the following:

- "finished or semi-finished" in claims 1 and 23, in the description on page 9, lines 4, 5 and 18;
- "between 0.4 and 7%" in claims 1 and 22, in the description on page 9, line 7;
- "mixture" in claim 7 (see originally filed description at page 17, line 26 where is disclosed "liquid");
- "further comprising an anion surfactant" in claim 10. The anionic surfactant is already claimed in claim 7 from which claim 10 depends.

### **3 NOVELTY**

- 3.1 The present application satisfy the criterion set forth in Article 33(2) PCT because the subject-matter of independent claims 1, 22 and 23 is new in respect to the prior art because none of the cited documents disclose the use of C<sub>12</sub>-C<sub>24</sub> alkanethiols, alkyl thioglycollate, dialkyl sulfide or dialkyl disulfide for treating silver alloys containing germanium.
- 3.2 Claims 2-21 are dependent on claim 1 and as such also meet the requirements of the PCT with respect to novelty.

### **4 INVENTIVE STEP**

- 4.1 The present application does not meet the criteria of Article 33(1) PCT, because the subject-matter of claims 1-6, 15-18, 22 and 23 does not involve an inventive step in the sense of Article 33(3) PCT.
- 4.2 The document D1 (the references in parentheses applying to this document) is regarded as being the closest prior art to the subject-matter of independent claims 1, 22 and 23 and shows the method to reduce tarnishing of silver and silver alloys by using alkanethiols or thioglycollates having 12 to 24 carbon atoms in the chain length as well as the article protected by this treatment (cf. col. 1, lines 38-41, col. 2, lines 26-33, 36-38, examples 1 and 2, claims 1-4 and 9-11). The subject-matter of claims 1, 22 and 23 of the present application differs from this known state of the art in that the treated silver alloys contain germanium.
- 4.3 Regarding the dialkyl disulfides as alternative treating agents, document D2 is considered to represent the most relevant state of the art and discloses the method to provide prolonged protection against tarnishing of silver alloys by using dialkyl sulfides, preferably distearyl disulfide, wherein the alkyl group has 8 to 22 , and preferably 12 to 22 carbon atoms as well as the article protected by this treatment (cf. col. 3, lines 15-37, 42-47, 51-53, examples 1, 3, 6, 7 and 8, claims 1-6).
- 4.4 With regard to the disclosure of D1 and D2 the problem to be solved by the present

invention may be regarded as reducing further the tarnishing.

- 4.5 This problem is solved by applying the treatment of D1 and/ or D2 to recently developed germanium containing silver alloys.
- 4.6 The skilled person would anyway use the known silver tarnish preventing treatments, including the ones disclosed in D1 and D2 to improve the tarnish resistance of the recently developed germanium containing silver alloys (see D4 and D5). Moreover, the fact that it is known from document D3, that the compounds used in D1 do form a protective layer on germanium is an additional indication that the treatment of D1 is very suitable for the claimed alloys.

Therefore, independent claims 1, 22 and 23 lack inventive step.

- 4.7 Dependent claims 2-6 and 15-18 do not appear to contain any additional features which, in combination with the features of any claim to which they refer, meet the requirements of the PCT in respect of inventive step, because these features are disclosed in one or more of the above cited documents or because no effect of the claimed feature is shown in the application.

- Claim 2: see point 4.2 and 4.3 above;
- Claim 3 and 4: see D1, example 1 and D2, example 6;
- Claim 5: no effect has been shown of the use of this solvent;
- Claim 6: see D2, example 7;
- Claim 15: see D1, example 1;
- Claim 16-18: known germanium containing silver alloys with improved tarnish resistance (see documents D4 and D5).

## **5 INDUSTRIAL APPLICABILITY**

- 5.1 The invention shall be considered as susceptible of industrial application because it can be used in the metal finishing industry.

**Re Item VIII**

**Certain observations on the international application**

- 1.1 The application does not meet the requirements of Article 6 PCT, because claims 1 and 10 are not clear.
- 1.2 It is clear from the document D2 (see column 3, line 42-47) that the chain length of the alkyl groups present in the organo-sulphur compounds (alkanethiol, alkyl thioglycollate, dialkyl sulfide or dialkyl disulfide) disclosed in claim 2 of the present application is essential to the definition of the invention.

Since independent claim 1 does not contain this feature it does not meet the requirement following from Article 6 PCT taken in combination with Rule 6.3(b) PCT, that any independent claim must contain all the technical features essential to the definition of the invention.

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**ENHANCING SILVER TARNISH-RESISTANCE****FIELD OF THE INVENTION**

5           The present invention relates to the use of organo-sulphur compounds in the enhancement of the tarnish resistance of silver alloys, to silver articles of enhanced tarnish resistance that have been surface-treated with the organo-sulphur compounds and to methods of keeping and display of the treated articles. It also relates to a water-based composition that can be used for the treatment of a  
10 metal which may be a silver alloy but which may also be another metal requiring surface treatment to impart tarnish resistance e.g. copper, brass or nickel.

**BACKGROUND TO THE INVENTION****15   Silver alloys and their tarnish-resistance**

          Standard Sterling silver provides manufacturers and silversmiths with a versatile and reliable material but it is inevitable that finished articles will require further cleaning and polishing to temporarily remove undesired tarnish products.  
20 It is well-known that with exposure to everyday atmospheric conditions, silver and silver alloys develop a lustre-destroying dark film known as tarnish.

          Since ancient times it has been appreciated that unalloyed 'fine' silver is too soft to withstand normal usage, and it has been the practice to add a  
25 proportion of a base metal to increase hardness and strength. In the UK, legislation that has existed since the fourteenth century specifies a minimum silver content of articles for sale at 92.5% (the Sterling standard), but does not specify the base metal constituents. Experience convinced early silversmiths that copper was the most suitable of the metals available to them. Modern silver-sheet  
30 manufacturers generally adhere to this composition, although sometimes a proportion of copper is replaced by cadmium to attain even greater ductility.



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Sterling with a 2.5% cadmium content is a standard material for spinning and stamping. Lower grades of silver alloys are common in many parts of Europe for the production of hollow-ware and cutlery. The 800-grade alloys (Ag parts per thousand) are predominantly used in southern and mid-Europe whereas in  
5 Scandinavia the 830 standard is predominant.

In all but the largest manufacturing companies, most of the annealing and soldering required to assemble finished or semi-finished articles is carried out with the flame of an air-gas blowtorch. The oxidising or reducing nature of the  
10 flame and the temperature of the articles are controlled only by the skill of the silversmith. Pure silver allows oxygen to pass easily through it, particularly when the silver is heated to above red heat. Silver does not oxidise in air, but the copper in a silver/copper alloy is oxidised to cuprous or cupric oxide. Pickling of the oxidised surface of the article in hot dilute sulphuric acid removes the superficial  
15 but not the deeper-seated copper oxide so that the surface consists of fine or unalloyed silver covering a layer of silver/copper oxide mixture. The pure silver is easily permeated during further heating, allowing copper located deeper below the surface to become oxidised. Successive annealing, cold working and pickling produces a surface that exhibits the pure lustre of silver when lightly polished but  
20 with heavier polishing reveals dark and disfiguring stains known as 'firestain' or 'fire'. Soldering operations are much more productive of deep firestain because of the higher temperatures involved. When the depth of the firestain exceeds about 0.025mm (0.010 inches) the alloy is additionally prone to cracking and difficult to solder because an oxide surface is not wetted by solder so that a proper  
25 metallurgical bond is not formed.

Patent GB-B-2255348 (Rateau, Albert and Johns; Metaleurop Recherche) disclosed a novel silver alloy that maintained the properties of hardness and lustre inherent in Ag-Cu alloys while reducing problems resulting from the tendency of  
30 the copper content to oxidise. The alloys were ternary Ag-Cu-Ge alloys containing at least 92.5 wt% Ag, 0.5-3 wt% Ge and the balance, apart from

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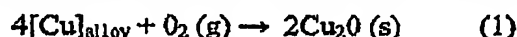
impurities, copper. The alloys were stated to be stainless in ambient air during conventional production, transformation and finishing operations, to be easily deformable when cold, to be easily brazed and not to give rise to significant shrinkage on casting. They were also stated to exhibit superior ductility and tensile strength and to be annealable to a required hardness. Germanium was stated to exert a protective function that was responsible for the advantageous combination of properties exhibited by the new alloys, and was in solid solution in both the silver and the copper phases. The microstructure of the alloy was said to be constituted by two phases, a solid solution of germanium and copper in silver surrounded by a filamentous solid solution of germanium and silver and copper. The germanium in the copper-rich phase was said to inhibit surface oxidation of that phase by forming a thin GeO or GeO<sub>2</sub> protective coating which prevented the appearance of firestain during brazing and flame annealing which results from the oxidation of copper at high temperatures. Furthermore the development of tarnish was appreciably delayed by the addition of germanium, the surface turned slightly yellow rather than black and tarnish products were easily removed by ordinary tap water. The alloy was said to be useful *inter alia* in jewellery. However, the alloy disclosed in the above patent suffers limitations insofar as it can exhibit large grain size, leading to poor deformation properties and formation of large pools from low-melting eutectics resulting in localised surface melting when the alloy is subject to the heat of an air torch.

Patents US-A-6168071 and EP-B-0729398 (Johns) disclose a silver/germanium alloy which comprised a silver content of at least 77 wt % and a germanium content of between 0.4 and 7%, the remainder principally being copper apart from any impurities, which alloy contains elemental boron as a grain refiner at a concentration of more than 0ppm and less than 20ppm. The boron content of the alloy can be achieved by providing the boron in a master copper/boron alloy having 2 wt % elemental boron. It was reported that such low concentrations of boron surprisingly provide excellent grain refining in a silver/germanium alloy, imparting greater strength and ductility to the alloy

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compared with a silver/germanium alloy without boron. The boron in the alloy inhibits grain growth even at temperatures used in the jewellery trade for soldering, and samples of the alloy were reported to have resisted pitting even upon heating repeatedly to temperatures where in conventional alloys the copper/germanium eutectic in the alloy would melt. Strong and aesthetically pleasing joints between separate elements of the alloy can be obtained without using a filler material between the free surfaces of the two elements and a butt or lap joint can be formed by a diffusion process or resistance or laser welding techniques. Compared to a weld in Sterling silver, a weld in the above-described alloy has a much smaller average grain size that improved the formability and ductility of the welds, and an 830 alloy has been welded by plasma welding and polished without the need for grinding.

Ternary and quaternary alloys e.g. Ag-Cu-Ge alloys and Ag-Cu-Zn-Ge alloys include two base metal alloying elements, Cu and Ge, in a noble parent metal, Ag. On exposure to an oxidising atmosphere, two oxidation reactions have to be considered. Firstly, the oxidation of copper to cuprous oxide:



Secondly, the oxidation of germanium to germanium (di)oxide:



The above equation shows formation of germanium (IV) oxide,  $\text{GeO}_2$ , but there may also be formed germanium (II) oxide,  $\text{GeO}$  or an intermediate material  $\text{Ge}_x\text{O}_y$  where  $x$  is 1 and  $y$  is greater than 1 but less than 2. Under standard conditions, i.e. for pure Cu and pure Ge each reacting with pure oxygen gas at 1 atm pressure to form the pure oxide phase, both reactions are feasible, with the chemical driving force for reaction (2) being higher than that of reaction (1) by a factor of 1.65.

According to WO 02/095082 (Johns) tarnish resistance of ternary alloys of silver, copper and germanium or quaternary alloys of silver, copper, zinc and germanium can be increased by casting a molten mixture to form the alloy and

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annealing the alloy to reduce its thickness and re-crystallize the grains in the alloy, the annealing being carried out under a selectively oxidizing atmosphere e.g.  $H_2/H_2O$  or  $CO/CO_2$  to promote the formation of  $GeO_2$  while preventing the formation of  $Cu_2O$ .

5

#### Treatment compositions for removing or preventing silver tarnish

Various proposals have been made for cleaning or protecting Sterling silver and other known grades of silver to remove tarnish and/or to inhibit the formation of tarnish.

10

US-A-2841501 discloses a silver polish based on an abrasive powder and a  $C_{12}$ - $C_{20}$  n-alkane thiol which is said to be non-toxic, to have a mild odor and to protect silver against tarnishing by forming a monomolecular layer  $R-S-Ag$  wherein R represents the alkane chain of the thiol, said layer forming a physical barrier between the silver and reactive ingredients of the atmosphere.

15

GB-A-1130540 is concerned with the protection of a finished surface of Sterling or Britannia silver as a step in a production run, and discloses a process that comprises the steps of:

20

wetting a clean silver surface of an article with a solution comprising 99 parts by weight of a volatile organic solvent, for example trichloroethylene or 1,1,1-trichloroethane and from 0.1-1.8 parts by weight of an organic solute containing a  $-SH$  group and capable of forming a transparent colourless protective layer on the silver surface, for example stearyl and cetyl mercaptan or thioglycollate;

25

allowing the solution to react with the surface to form such a layer and allowing the solvent to evaporate; and

30

washing the surface with a detergent solution, rinsing the surface with hot water and allowing it to dry. The above process is stated to provide a "long-term finish" intended to last the intended shelf-life until the article reaches the user.

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Halohydrocarbons were said to be the most suitable solvents but their suitability on environmental grounds is now open to question. Ethers were said to be flammable and toxic, and lower alcohols were said to be poor solvents. Water is not mentioned as a solvent. Applicants have seen a report on the Internet from

5 ATOFINA Chemicals Inc that the solubility of mercaptans in water decreases progressively from 23.30 g/litre for methyl mercaptan to 0.00115 g/litre for nonyl mercaptan, and data for both hexadecyl and octadecyl mercaptan (CAS 2885-00-9) reports them as water-insoluble.

10 US-A-6183815 (Enick) also teaches that treatments of the above kind are result in the formation of a self-assembled coating derived from the thiol compounds in which the sulphur atoms are bound onto the metal surface and the alkyl tails are directed away from the metal surface. In the examples of that specification, fluoroalkyl amides e.g.  $\text{CF}_3(\text{CF}_2)_5\text{CONH}(\text{CH}_2)_2\text{SH}$  in aqueous

15 alcohols e.g. aqueous isopropanol are sprayed onto the surface of silver, after which the surface is rinsed and dried with a soft cloth. The fluoroalkyl amides lack detectable odour and can dissolve in lower alcohols or alcohol/water mixtures, although it is apparent from the description and examples that not all alcoholic solvents produce good films.

20 Yousong Kim *et al* report that the adsorption of thiols onto silver proceeds through an anodic oxidation reaction that produces a shift of the open circuit potential of the substrate metal in the negative direction or if the potential is fixed an anodic current peak:

25  $\text{RSH} + \text{M}(0) \rightarrow \text{RS-M(I)} + \text{H}^+ + \text{e}^-(\text{M})$  (M = Au or Ag), see  
<http://www.electrochem.org/meetings/past/200/abstracts/symposia/h1/1026.pdf>

Kwan Kim, *Adsorption and Reaction of Thiols and Sulfides on Noble Metals*, Raman SRS-2000, 14-17 August 2000, Xiamen, Fujian, China,

30 <http://pcoss.org/icorsxm/paper/kuankim.pdf>, also discloses the formation of self-assembled monolayers and discloses that alkanethiols, dialkyl sulfides and dialkyl

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disulfides self-assemble on silver surfaces with aliphatic dithiols forming dithiolates by forming two Ag-S bonds.

In contrast, the literature on formation of alkylthiols of germanium is relatively sparse. The dissociative adsorption of H<sub>2</sub>S at a Ge 100 surface to yield adsorbed -SH groups and adsorbed hydrides has been reported by Nelen *et al.*, *Applied Surface Science*, 150, 65-72 (1999), see <http://www.chem.missouri.edu/Greenlief/pubs/00005797.pdf>, see also a report by Professor Michael Greenlief of the University of Missouri-Columbia <http://www.chem.missouri.edu/Greenlief/Research.html> that room temperature exposure of H<sub>2</sub>S to Ge(100) results in dissociative adsorption that can be followed easily by ultraviolet photoelectron spectroscopy. The reaction of alkanethiols with Ge to form a high quality monolayer has been reported in the context of semiconductor and nanotechnology by Han *et al.*, *J. Am. Chem. Soc.*, 123, 2422 (2001). In the experiment described, a Ge(111) wafer is sonicated in acetone to dissolve organic contaminants and immersed in concentrated HF to remove residual oxide and produce a hydrogen-terminated surface, after which the wafer is immersed in an alkanethiol solution in isopropanol, sonicated in propanol and dried.

#### SUMMARY OF THE INVENTION

Although GB-A-1130540 was alleged to provide a long-term finish, the experience of one of the inventors who is a silversmith is this type of treatment does not fully solve the difficulties created by tarnish in the period between manufacture and supply to the ultimate purchaser or user and suffers from a number of shortcomings. Although a silver product might arrive at the retailer in an untarnished state, it was largely the result of the wrapping applied by the manufacturer, which protected the article from air. Once the wrapping was removed and the article was displayed in a retail environment such as a display case in a hotel where it was subject to ambient air and the heat of artificial

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lighting, an article of conventional Sterling silver would require re-polishing after one week and after two weeks would normally be so tarnished as to be un-saleable. At an exhibition, the life of an article on display before significant tarnish sets in may be as short as 3-4 days. Re-polishing produces wear and fine handling scratches, so that unless the article can be sold quickly it loses its pristine appearance. The need to polish display silver at frequent intervals adds to the labour cost of a jeweller or other retail establishment, whose management take the view that its staff should be employed to sell products and not to clean stock. Tarnish at point of sale or display is therefore a serious problem that reduces the willingness of those in the distribution chain to stock and display silver products, and which has not yet been adequately solved.

When the product reaches the ultimate purchaser, it is of course desirable that the task of tarnish removal should be made as infrequent and undemanding as possible.

Silver alloys according to the teaching of GB-B-2255348 and EP-B-0729398 are now commercially available in Europe and in the USA under the trade mark Argentium, and the word "Argentium" as used herein refers to these alloys. Although they exhibit improved tarnish resistance compared to e.g. Sterling silver, and any tarnish that forms can be removed by simple washing, there is still room for improvement in tarnish resistance. That remains true even when annealing is conducted in a selectively oxidising atmosphere as disclosed in WO 02/095082.

It has now been found that an alkanethiol, alkyl thioglycolate, dialkyl sulphide or dialkyl disulphide can be used for the surface treatment of an alloy of silver containing an amount of germanium that is effective to reduce firestain and/or tarnishing so as to reduce or further reduce tarnishing of the alloy such that a sample can be subjected to hydrogen sulphide gas above a 20% solution of

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ammonium polysulphide for at least 30 minutes and typically 45-60 minutes at room temperature while retaining a generally untarnished appearance.

5 The invention therefore relates to a method for treating a finished or semi-finished shaped flatware, hollowware or jewellery article of a silver/germanium alloy that has a silver content of at least 77 wt % and a germanium content of between 0.4 and 7% the remainder principally being copper so as to reduce or further reduce tarnishing of the article such that a sample of the alloy of which the article is made can be supported close above a 20% solution of ammonium  
10 polysulphide for at least 30 minutes while retaining a generally untarnished appearance, said method comprising

surface treating said article with an alkanethiol, alkyl thioglycollate, dialkyl sulfide or dialkyl disulfide

15 The above method may include the further step of introducing the article into packaging.

The invention further provides a finished or semi-finished shaped flatware, hollowware or jewellery article of an alloy of silver containing an  
20 amount of germanium that is effective to reduce firestain and/or tarnishing and that has been treated with a C<sub>12</sub>-C<sub>24</sub> alkanethiol, alkyl thioglycollate, dialkyl sulphide or dialkyl disulphide and that exhibits a tarnish resistance such that a sample of the alloy of which the article is made can be supported close above a 20% solution of ammonium polysulphide for at least 30 minutes while retaining a  
25 generally untarnished appearance.

The above accelerated tarnish test in which the article is subject to hydrogen sulphide gas from the ammonium polysulphide solution above which it is suspended at a height of e.g. 30mm corresponds to a period of a year or more in  
30 a retail environment where an article is on display and exposed to ambient atmosphere and may be subject to elevated temperatures. It is the combination of



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the protective function of the germanium content of the alloy with the further protection from the organo-sulphur compound that is believed to be responsible for the observed increase in tarnish resistance. The period during which the article retains its untarnished appearance under these severe conditions may be three or more times the corresponding period for an article that has not been treated with an organo-sulphur compound, which is unexpected because the same accelerated tarnish test carried out under the same conditions on a conventional Sterling silver article not containing protective germanium does not reveal a significant increase in untarnished lifetime between its untreated and organo-sulfur treated states.

Accelerated tarnishing trials carried out using Argentium and standard Sterling silver samples immersed in solutions of octadecyl mercaptan and hexadecyl mercaptan have shown that the protective thiol is removed from the standard Sterling sample but not from the Argentium silver samples on rubbing with a tissue soaked in a solvent (EnSolv 765, an n-propyl bromide based solvent cleaner discussed below). In accelerated testing the solvent-rubbed regions of standard Sterling silver discolour more rapidly than the un-rubbed regions whereas in Argentium silver no noticeable difference in appearance develops between the rubbed and un-rubbed regions, suggesting that thiol bonding is stronger or more effective.

20

Accelerated tarnishing tests with Argentium Sterling using ammonium polysulphide have been reported by the Society of American Silversmiths, see <http://www.silversmithing.com/Argentium4.htm> and in a comparative test the Argentium Sterling remained untarnished after one hour whereas conventional Sterling became tarnished after less than 15 minutes. However, in this test 0.5ml of 20% ammonium polysulfide solution is mixed with 200ml of distilled water, so that the test is greatly less severe than when samples are exposed to the 20% solution itself. In WO 02/095082, samples were suspended above 20% ammonium polysulphide, but the exposure times were relatively short, and onset of yellowing was reported for Ag-Cu-Ge alloys after 3-5 minutes exposure. Other tests reported in that specification involve placing

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samples in a desiccator containing flowers of sulphur and calcium nitrate and are less severe than the ammonium polysulphide test.

5 As part of their program for developing improved formulations for the treatment agents described above, the applicants have unexpectedly discovered that the treatment agents can be dissolved or dispersed directly in aqueous surfactant without the need for preliminary dissolving of the treatment agent in an organic solvent and subsequent mixing of the resulting solution with aqueous liquid. Embodiments of the above compositions are optically clear and storage-  
10 stable at ambient temperatures for a period of weeks or months. The treatment composition may therefore be water-based and comprise an alkanethiol, alkyl thioglycollate, dialkyl sulfide or dialkyl disulfide and a mixture of an anionic surfactant with a neutral or amphoteric surfactant and water.

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## DETAILED DESCRIPTION OF THE INVENTION

## Silver-copper-germanium alloys

5           The alloys that may be treated according to the invention include an alloy of silver containing an amount of germanium that is effective to reduce firestain and/or tarnishing. US-A-6406664 (Diamond) discloses that amounts of germanium as low as 0.1wt% can be effective provided that substantial amounts of tin are present but although formulation examples are given, no test data for  
10 corrosion or firestain is given either for articles made by casting or for articles fabricated from sheet. The inventor considers that 0.5 wt% Ge provides a preferred and more realistic lower limit and that in practice use of less than 1wt% is undesirable. A two-component copper-free alloy could comprise 99% Ag and 1 % Ge, and a tarnish-free casting alloy for jewellery has been reported that  
15 comprises 2.5%Pt, 1% Ge, balance Ag and optionally containing Zr, Si or Sn.

          The ternary Ag-Cu-Ge alloys and quaternary Ag-Cu-Zn-Ge alloys that can suitably be treated by the method of the present invention are those having a silver content of at least 30%, preferably at least 60%, more preferably at least  
20 80%, and most preferably at least 92.5%, by weight of the alloy, up to a maximum of no more than 98%, preferably no more than 97%. The germanium content of the Ag-Cu-(Zn)-Ge alloys should be at least 0.1%, preferably at least 0.5%, more preferably at least 1.1%, and most preferably at least 1.5%, by weight of the alloy, up to a maximum of preferably no more than 6.5%, more preferably  
25 no more than 4%.

          If desired, the germanium content may be substituted, in part, by one or more elements which have an oxidation potential selected from Al, Ba, Be, Cd, Co, Cr, Er, Ga, In, Mg, Mn, Ni, Pb, Pd, Pt, Si, Sn, Ti, V, Y, Yb and Zr, provided  
30 the effect of germanium in terms of providing firestain and tarnish resistance is not unduly adversely affected. The weight ratio of germanium to substitutable

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elements may range from 100: 0 to 60: 40, preferably from 100: 0 to 80: 20. Preferably, the germanium content consist entirely of germanium, i. e. the weight ratio is 100: 0.

5           The remainder of the ternary Ag-Cu-Ge alloys, apart from impurities and any grain refiner, will be constituted by copper, which should be present in an amount of at least 0.5%, preferably at least 1%, more preferably at least 2%, and most preferably at least 4%, by weight of the alloy. For an '800 grade' ternary alloy, for example, a copper content of 18.5% is suitable. The remainder of the  
10       quaternary Ag-Cu-Zn-Ge alloys, apart from impurities and any grain refiner, will be constituted by copper which should be present in an amount of at least 0.5%, preferably at least 1%, more preferably at least 2%, and most preferably at least 4%, by weight of the alloy, and zinc which should be present in a ratio, by weight, to the copper of no more than 1: 1. Therefore, zinc is optionally present in the  
15       silver-copper alloys in an amount of from 0 to 100 % by weight of the copper content. For an '800 grade' quaternary alloy, for example, a copper content of 10.5% and zinc content of 8% is suitable.

20           In addition to silver, copper and germanium, and optionally zinc, the alloys preferably contain a grain refiner to inhibit grain growth during processing of the alloy. Suitable grain refiners include boron, iridium, iron and nickel, with boron being particularly preferred. The grain refiner, preferably boron, may be present in the Ag-Cu-(Zn)-Ge alloys in the range from 1 ppm to 100 ppm, preferably from 2 ppm to 50 ppm, more preferably from 4 ppm to 20 ppm, by  
25       weight of the alloy.

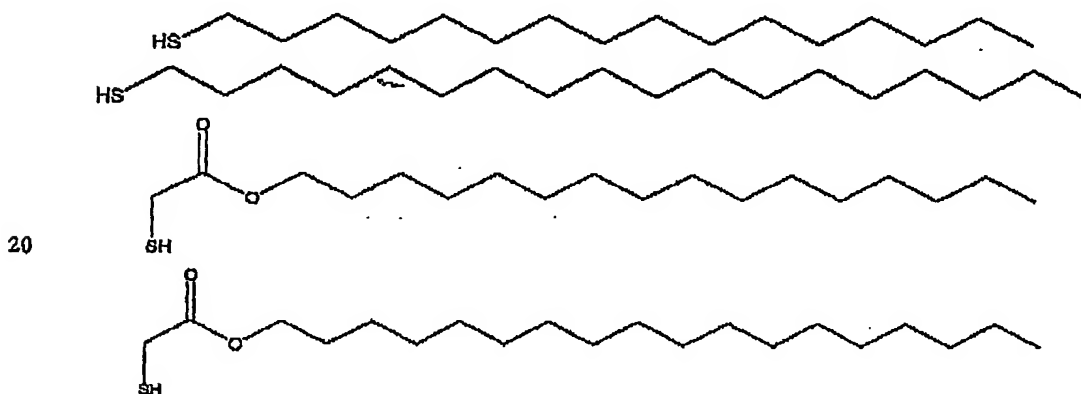
30           In a preferred embodiment, the alloy is a ternary alloy consisting, apart from impurities and any grain refiner, of 80% to 96% silver, 0.1 % to 5% germanium and 1 % to 19.9% copper, by weight of the alloy. In a more preferred embodiment, the alloy is a ternary alloy consisting, apart from impurities and grain refiner, of 92.5% to 98% silver, 0.3% to 3% germanium and 1% to 7.2%

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copper, by weight of the alloy, together with 1 ppm to 40 ppm boron as grain refiner. In a further preferred embodiment, the alloy is a ternary alloy consisting, apart from impurities and grain refiner, of 92.5% to 96% silver, 0.5% to 2% germanium, and 1% to 7% copper, by weight of the alloy, together with 1 ppm to 40 ppm boron as grain refiner.

### Protective agents

As protective agent there may be used a compound containing a long chain alkyl group and a -SH or -S-S- group, e.g. an alkanethiol, dialkyl sulfide or dialkyl disulfides in which the chain is preferably at least 10 carbon atoms long and may be C<sub>12</sub>-C<sub>24</sub>. The -SH or -S-S- compounds that may be used include straight chain saturated aliphatic compounds containing 16-24 carbon atoms in the chain, for example octyl mercaptan (hexadecyl mercaptan) and stearyl mercaptan (octadecyl mercaptan) and cetyl and stearyl thioglycollates whose formulae appear below.



Octadecyl mercaptan is a white to pale yellow waxy solid that is insoluble in water and that melts at 15-16°C. Hexadecyl mercaptan is also a white or pale yellow waxy solid that melts at 30°C.

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**Formulations based on organic solvents**

The protective agent may be used in solution in a solvent e.g. a non-polar organic solvent such as an alcohol e.g. methyl or ethyl alcohol, a ketone e.g. acetone or methyl ethyl ketone, an ether e.g. diethyl ether, an ester e.g. n-butyl acetate, a hydrocarbon, a halocarbon e.g. methylene chloride, 1,1,1-trichloroethane, trichloroethylene, perchloroethylene or HCFC 141b. The protective agent may comprise 0.1-1 wt% of the solvent. Solvents based on alkyl or aryl halides may be used e.g. n-propyl bromide which is presently preferred on the ground of the short atmospheric life of that compound, its relatively low toxicity compared to other halocarbons, its favourable chemical and physical properties and its boiling point, specific heat and latent heat of vaporization.

US-A-5616549 discloses a solvent mixture comprising: 90 percent to about 96.5 percent n-propyl bromide; 0 percent to about 6.5 percent of a mixture of terpenes, the terpene mixture comprising 35 percent to about 50 percent cis-pinane and 35 percent to about 50 percent trans-pinane; and 3.5 percent to about 5 percent of a mixture of low boiling solvents, the low boiling solvent mixture comprising 0.5 percent to 1 percent nitromethane, 0.5 percent to 1 percent 1,2-butylene oxide and 2.5 percent to 3 percent 1,3-dioxolane. The solvent mixture has the following advantages:

(i) it is properly stabilized against any free acid that might result from oxidation of the mixture in the presence of air, from hydrolysis of the mixture in the presence of water, and from pyrolysis of the mixture under the influence of high temperatures;

(ii) it is non-flammable and non-corrosive;

(iii) the various components of the solvent mixture are not regulated by the U.S. Clean Air Act; and

(iv) none of the various components of the solvent mixture are known cancer causing agents (i.e., the various components are not listed by N.T.I., I.A.R.C. and California Proposition 65, nor are they regulated by OSHA).

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Moreover, the solvent mixture has a high solvency with a kauri-butanol value above 120 and, more preferably, above 125. In addition, the solvent mixture has an evaporation rate of at least 0.96 where 1,1,1-Trichloroethane=1. Upon evaporation, the solvent mixture leaves a non-volatile residue (NVR) of less than 2.5 mg and, more preferably, no residue. Solvents made in accordance with the above patent are available from Enviro-Tech International, Inc of Melrose Park, Illinois, USA under the trade name EnSolv.

#### Formulations based on organic solvent and water

For many purposes, e.g. light industrial applications, it may be preferred to carry out the anti-tarnish treatment using a predominantly aqueous solvent system. For this purpose, the protective agent may be dissolved in a water-immiscible organic solvent, for example a solvent based on *n*-propyl bromide, the resulting solution may be mixed with a relatively concentrated water-based soap or detergent composition which acts as a "carrier", after which water is added to the resulting mixture to provide an aqueous treatment dip or combined degreasing and treatment solution. Thus an aqueous dip has the advantages that a solvent degreasing system is not necessary, the dip is easily made and may be used cold, all areas of immersed articles can come into contact with the stearyl mercaptan or other treatment agent, Argentium Silver only requires 2 minutes – 1 hour in the dip, rinsing and drying of articles are made easy as water droplets are repelled from the surface of the polished silver, and the dip can be easily used in a manufacturing environment before articles are sent to retailers.

Preferred water-based detergents may be based on anionic, alkoxylated non-ionic or water-soluble cationic surface active agents or mixtures of them and preferably have a pH at or close to 7. Anionic surfactants may be based on alkyl sulphates and alkyl benzene sulphonates, whose harshness on prolonged skin exposure may be reduced by the co-presence or use of alkyl ethoxy sulphates (US-A-3793233, Rose *et al.*; 4024078 Gilbert; 4316824 Pancherni). Other known

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surfactants e.g. betaines may also be present, see e.g. US-A-4555360 (Bissett). A suitable formulation containing 5-15 wt% non-ionic surfactants and 15-30 wt% anionic surfactants is available commercially in the UK under the trade name Fairy Liquid (Proctor & Gamble).

5

An aqueous liquid may also be made by dissolving the treatment agent in a non-organic solvent and adding a relatively concentrated aqueous detergent liquid, for example undiluted Fairy Liquid. This provides a detergent liquid that has a number of advantages: the soapy liquid is easily made, the liquid is easily  
10 applied to the Argentium Silver articles with a damp sponge/cotton wool/cloth etc., the liquid and lather enables the stearyl mercaptan or other treatment agent to get into those awkward areas on an article where a cloth may not be able to reach, rinsing and drying of articles are made easy as water droplets are repelled from the surface of the polished silver, the process can be easily used in a  
15 manufacturing environment before articles are sent to retailers and can also be easily used in a retail or domestic environment. Furthermore, the hydrophobic properties imparted to silver/silver alloy on treatment with the present thiol-based treatment agents may alleviate or overcome the problems of water-marks or water-staining from rinsing processes in a manufacturing or domestic  
20 environment.

#### Formulations based on aqueous liquids

It has surprisingly been found that formulations containing effective  
25 amounts of the treatment agents can be made by dissolving them directly in aqueous liquids containing an anionic and a neutral or amphoteric surfactant and free from water-immiscible organic solvents and preferably free from all other solvents. The treatment agents may be dissolved in relatively concentrated surfactant-containing aqueous liquids, which may be used as such or after  
30 subsequent dilution with water, see in particular the instructions given in the preceding section.



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The treatment agent may be present in said composition, prior to dilution thereof, in an amount of at least 0.1 wt % and preferably at least 1 wt %, the solids content of the composition being at least 5 wt %, typically 10-40 wt % and possibly 50 wt% or more. The ability of aqueous surfactant liquids to dissolve or disperse such relatively high concentrations of higher alkyl thiols and other treatment agents which are reported to be highly water-insoluble has not been described. The resulting concentrates may be diluted with water to provide an aqueous treatment dip or combined degreasing solution and dip for use as explained above, and it has been found that the treatment agent may remain in solution or suspension following such dilution and may remain effective for the surface treatment of silver-copper or silver-copper-germanium alloys and possibly other metals such as copper, brass and nickel where surface protection films may retard corrosion. Particularly good results from the stability and effectiveness standpoint may be obtained by mixing hexadecyl mercaptan (in the liquid state) straight into a surfactant "carrier" and using the solution as such or on subsequent dilution with water.

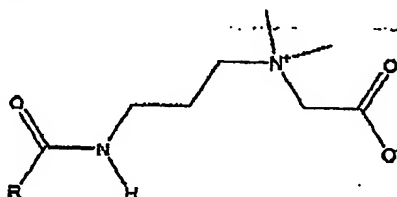
In particular, the present treatment agents can be successfully dispersed in aqueous liquids containing mixtures of neutral and anionic surfactants with the neutral surfactants providing e.g. about 33 wt% of the total surfactant present. Treatment agents that can be dispersed in such agents include n-hexadecyl thiol and n-octadecyl thiol. They can also be successfully dispersed in aqueous liquids containing mixtures of amphoteric or zwitterionic surfactants and anionic surfactants and such mixtures can provide relatively storage stable optically clear solutions with little or no tendency to re-precipitate the treatment agent. In that case the weight ratio of the amphoteric or zwitterionic surfactant to the anionic surfactant may be from 1:10 to 10:1, typically close to 1:3.

Amphoteric or zwitterionic surfactants that may be used alone or in admixture with one another and/or with nonionic surfactants and/or with anionic surfactants may be derivatives of secondary or tertiary amines, derivatives of

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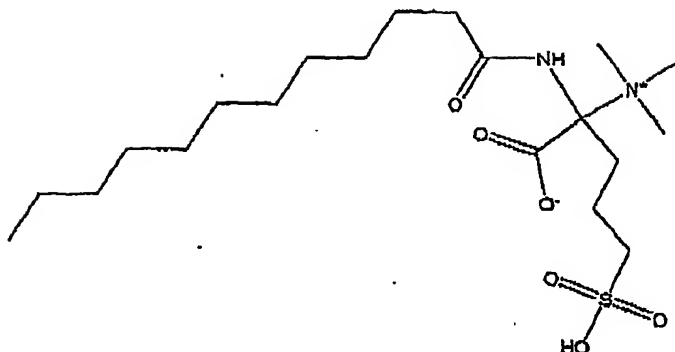
heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. The cationic atom in the quaternary compound can be part of a heterocyclic ring. In all of these compounds there is at least one aliphatic group, straight chain or  
5 branched, containing from about 3 to 18 carbon atoms and at least one aliphatic substituent containing an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate.

Examples of zwitterionic surfactants that may be employed include  
10 betaine surfactants, which are preferred, imidazoline-based surfactants, aminoalkanoate surfactants and iminodialkanoate surfactants. Suitable such surfactants include amidocarboxybetaines, such as cocoamidodimethylcarboxymethylbetaine, laurylamidodimethylcarboxymethylbetaine, cetylamidodimethylcarboxy-methylbetaine, and cocoamido-bis-(2-  
15 hydroxyethyl)carboxymethylbetaine. Particularly preferred are amidocarboxybetaines of the formula below wherein R represents C<sub>8</sub>-C<sub>18</sub> alkyl e.g. cocamidopropyl betaine. That compound is generally regarded as safe: in an Ames test conducted by BASF it did not prove mutagenic to Salmonella indicator organisms and in a human repeated patch insult test (HRIPT) it did not  
20 indicate either contact hypersensitivity or photoallergy (see the MAFO CAB cocamidopropyl amino betaine data sheet published by BASF):



Also useful are sulphobetaine surfactants, e.g. amido sulfobetaines such as  
25 lauramido-sulfopropylbetaine of formula indicated below,

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cocamido-2-hydroxypropylsulfobetaine, cocoamidodimethylsulfopropylbetaine, stearyl-amido-dimethylsulfopropylbetaine, and laurylamido-bis-(2-hydroxyethyl)-sulfopropylbetaine. Also useful may be imidazoline-based surfactants including glycinate and amphoteric compounds e.g. cocoamphocarboxypropionate, cocoamphocarboxypropionic acid, cocoamphocarboxyglycinate, and cocoamphoacetate, aminoalkanoate surfactants e.g. n-alkylamino-propionates and n-alkyliminodipropionates such as N-lauryl- $\beta$ -amino propionic acid and salts thereof, and N-lauryl- $\beta$ -imino-dipropionic acid and salts thereof.

10

Non-ionic surface-active agents that may be used alone or in admixture include compounds produced by the condensation of an alkylene oxide with an organic hydrophobic compound that may be aliphatic or alkyl aromatic. The length of the hydrophilic or polyoxyalkylene moiety that is condensed with any particular hydrophobic compound can be adjusted to yield a water-soluble compound having the desired balance between hydrophilic and hydrophobic moieties. Semi-polar nonionic surface active agents may also be used, including amine oxides, phosphine oxides, and sulfoxides. Suitable classes of compound include:

- 20
- Polyethylene oxide condensates of alkyl phenols. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to 12 carbon atoms in either a straight or branched chain, with ethylene oxide, the said ethylene oxide being present in amounts equal to 5 to 25 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in

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such compounds may be derived, for example, from polymerized propylene, diisobutylene, octene, or nonene.

- Condensation products of aliphatic alcohols with ethylene oxide. The alkyl chain of the aliphatic alcohol may either be straight or branched and generally contains from about 8 to about 22 carbon atoms.
- Condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine.
- Amine oxide surfactants, for example dimethyldodecylamine oxide, dimethyltetradecylamine oxide, ethylmethyltetradecylamine oxide, cetyldimethylamine oxide, dimethylstearylamine oxide, cetyl ethylpropylamine oxide, diethyldodecylamine oxide, diethyltetradecylamine oxide, dipropyldodecylamine oxide, bis-(2-hydroxyethyl)dodecylamine oxide, bis-(2-hydroxyethyl)-3-dodecoxy-2-hydroxypropylamine oxide, (2-hydroxypropyl)methyltetradecylamine oxide, dimethyloleylamine oxide, dimethyl-(2-hydroxydodecyl)amine oxide, and the corresponding decyl, hexadecyl and octadecyl homologs of the above compounds.
- Phosphine oxide surfactants, e.g. dimethyldodecylphosphine oxide, dimethyltetradecylphosphine oxide, ethylmethyltetradecylphosphine oxide, cetyldimethylphosphine oxide, dimethylstearylphosphine oxide, cetyl ethylpropylphosphine oxide, diethyldodecylphosphine oxide, diethyltetradecylphosphine oxide, dipropyldodecylphosphine oxide, dipropyldodecylphosphine oxide, bis-(hydroxymethyl)dodecylphosphine oxide, bis-(2-hydroxyethyl)dodecylphosphine oxide, (2-hydroxypropyl)methyltetradecylphosphine oxide, dimethyloleylphosphine oxide, and dimethyl-(2-hydroxydodecyl)phosphine oxide and the corresponding decyl, hexadecyl, and octadecyl homologs of the above compounds.
- Sulfoxide surfactants, for example octadecyl methyl sulfoxide, dodecyl methyl sulfoxide, tetradecyl methyl sulfoxide, 3-hydroxytridecyl methyl sulfoxide, 3-methoxytridecyl methyl sulfoxide, 3-hydroxy-4-dodecoxybutyl

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methyl sulfoxide, octadecyl 2-hydroxyethyl sulfoxide, and dodecylethyl sulfoxide.

- Ethanolamide-based surfactants e.g. coconut fatty acid monoethanolamide or diethanolamide.

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wherein R represents C<sub>10</sub>-C<sub>40</sub>, esp C<sub>12</sub>-C<sub>18</sub> alkyl e.g. oleyl- or coco-. Further surfactants may be based on diethylene triamine (DETA)-based quaternaries, such as diamidoamine ethoxylates and imidazolines, and esterquats. As a class, esterquats can be based on compounds including methyl diethanolamine (MDEA), triethanolamine (TEA), and N,N-dimethyl-3-aminopropane-1,2-diol (DMAPD).

10

A wide variety of alkyl sulfates may be used as anionic surface-active agents including fatty alcohol sulphates, fatty alcohol ether sulphates, alkyl phenol ether sulphates, alkyl aryl sulphonic acids and salts thereof, cumene, toluene and xylene sulphonates and salts thereof and alkyl sulphosuccinates e.g. sodium or ammonium lauryl sulfate. However, a preferred class of anionic surface active agents is polyol monoalkylether sulfates of the formula RO-(CH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>SO<sub>3</sub>M wherein R represents C<sub>10</sub>-C<sub>18</sub> alkyl, n is 2-6 (preferably about 2-3) and M represents a monovalent cation. Such compounds are sulfonated ethoxylated C<sub>10</sub>-C<sub>18</sub> alcohols which may be derived from coconut oil or tallow or may be synthetic. Sodium laureth sulfate which has been used successfully herein is a sodium lauryl ether sulphate ethoxylated to an average of two moles of ethylene oxide per mole of lauric acid and sulfated, and is of formula

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In addition to simple treatment agents, the above compositions may be formulated into metal polishes e.g. for silver or brass. Such products may be formulated as liquid products into which objects such as jewellery or cutlery are to be dipped. After dipping, the objects are usually rinsed under water and dried

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with a soft cloth. Alternative formulations take the form of creams or papes which are applied with a soft cloth and then removed.

For formulation into dipping compositions, the active ingredients are normally an acid having a pKa of not more than 5, e.g. phosphoric, citric, oxalic, or tartaric acid together with thiourea or a derivative thereof e.g. an alkyl derivative such as methyl or ethyl thiourea. For formulation into creams or pastes there may be e.g. about 25 wt% of a mild abrasive such as precipitated chalk, infusorial earth, silica or  $\gamma$ -alumina (e.g. 0.05  $\mu\text{m}$  grade). These ingredients are believed compatible with the surfactants and treatment agents and can be incorporated when convenient by simple mixing.

#### Treatment procedures

The surface treatment may be carried out after the manufacturing stages for a shaped article made of the alloy have been completed. The article may be of flatware, hollowware or jewellery. Fabrication steps may include spinning, pressing, forging, casting, chasing, hammering from sheet, planishing, joining by soldering brazing or welding, annealing and polishing using buffs/mops and aluminium oxide or rouge.

An article to be treated may be de-greased by various methods:

- Vapour degreasing with or without ultrasonics
- Aqueous degreasing with or without ultrasonics
- Organic solvent degreasing with or without ultrasonics (e.g. degreasing with ethanol or acetone prior to thiol treatment which may provide very good accelerated tarnish test results).
- Simultaneous degreasing and thiol treatment, the thiol being present in an organic or aqueous degreasing medium.

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For example, the article may be degreased ultrasonically in a treatment bath, dipped into a bath containing the treatment agent e.g. 1 wt% stearyl mercaptan in solvent e.g. EnSolv, rinsed in one or more baths of the solvent and allowed to dry by evaporation. Rinsing excess thiol away with the same solvent  
5 that is used for thiol treatment is preferred, so that thiols that have not reacted with the metallic surface are removed and are unavailable to react with anything else. The solvent should leave no or substantially no residue, so that subsequent washing with water or aqueous solvents should be unnecessary and the article can be allowed to dry. The article may then be packed for delivery into the  
10 distribution chain. This may include wrapping the article in one or more protective sheets, placing it in a presentation box, and wrapping the presentation box in a protective wrapping e.g. of heat-shrunk plastics film. Articles which have been treated with an organic compound containing -SH or -S-S- groups as  
15 aforesaid and packaged should not only reach their point of sale in good condition but should if displayed e.g. on a shelf or in a cabinet for an extended period, expected to be at least 6 months and possibly 12 months or more, remain without development of significant tarnish.

The articles may alternatively simply be polished with a polish containing  
20 1-5wt% of the organo-sulphur compound e.g. stearyl mercaptan together with surfactants and a cleaning agent e.g. diatomaceous earth in a solvent. As a further alternative, they may be simply polished with a cloth impregnated with the organo-sulphur compound e.g. cetyl or stearyl mercaptan e.g. by impregnation  
25 with a treatment agent in an organic solvent e.g. n-propyl bromide followed by drying. The advantages of a cleaning cloth are that it is easily manufactured, can be easily used in a retail or domestic environment and is good for general upkeep of Argentium Silver (if required).

The treatment method of the invention would find particular benefit in the  
30 tarnish protection of blanks for stamping coins immediately before the stamping operation because it has been found that embodiments of the present films can

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largely or wholly survive the stamping operation and can provide protection against tarnishing for the newly minted coins. It will be appreciated that coins in mint condition are packaged for collectors with minimal handling, and that every occasion of handling e.g. polishing with a soft cloth involves risk of damage to the coin. The risk of such damage is reduced by the present treatment which can impart prolonged tarnish resistance.

The invention will now be further described, by way of illustration only, with reference to the following examples. Throughout the examples, the term "enhanced tarnish resistance" of samples treated with stearyl mercaptan refers to the comparison with samples of Argentium Silver which have not had any treatment except for polishing and degreasing.



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### Example 1

#### Solvent dip application (solvent degreased samples)

5        Solutions were made up containing stearyl mercaptan (0.1, 0.5 and 1.0 gram) in EnSolv 765 (100 ml). Samples of Argentium Sterling which had been polished and ultrasonically degreased in EnSolv 765 for 2 minutes were each immersed in one of the stearyl mercaptan solutions for periods of 2 minutes, 5 minutes and 15 minutes. The samples were then buffed with clean cotton wool.

10

      - In order to evaluate tarnish resistance, the alloy samples were supported on a glass slide in a fume cupboard about 25mm above the surface of 20% ammonium polysulphide solution so as to be exposed to the hydrogen sulphide that arises from that solution. All of the samples demonstrated good tarnish  
15        resistance during a one-hour test, with very slight yellowing after 45 minutes exposure to the hydrogen sulphide. The light film on the samples was easily removed with a cleaning cloth impregnated with stearyl mercaptan.

      By way of comparison, a standard Sterling silver sample started to  
20        discolour as soon as it was subjected to the above test and after one hour had formed a heavy black tarnish which could not be removed with a cleaning cloth impregnated with stearyl mercaptan. The results obtained with a second Sterling silver sample that had been wiped with the cleaning cloth were similar and discoloration started as soon as the sample had been placed into the test. An  
25        Argentium Sterling alloy produced in accordance with EP-B-0729398 showed onset of tarnishing after 3 minutes. Another sample of the Argentium Sterling alloy that had been annealed in a selectively oxidizing atmosphere as disclosed in WO 02/09502 showed onset of tarnishing after 6 minutes. The markedly increased delay in onset of tarnishing was unexpected in the absence of an  
30        increased delay in the case of the standard Sterling Silver article.

### Example 2

5 Example 1 was repeated for the Argentium samples except that instead of buffing with cotton wool after the mercaptan treatment, the samples were ultrasonically degreased in EnSolv 765 for 2 minutes. The samples were then tarnish tested as described in Example 1 and all found to show enhanced tarnish resistance. The ability of the protective effect of the stearyl mercaptan treatment to survive ultrasonic cleaning in EnSolv suggests that the tarnish resistance is  
10 being achieved by a surface reaction involving the stearyl mercaptan and possibly the germanium in the Argentium Silver, and not by formation of a grease or oil layer on the surface of the Argentium.

**Aqueous dip application (solvent degreased samples)**

20      An anti-tarnish treatment solution was prepared using the following ingredients:

	Stearyl mercaptan	1g
	EnSolv 765	5 ml
	Detergent (Fairy Liquid)	40 ml
25	De-ionised water	100 ml

The Stearyl Mercaptan was dissolved into the EnSolv 765 after which the resulting solution was mixed with detergent (Fairy Liquid) and diluted with water to provide an aqueous dip. Samples of Argentium silver were polished and 30 ultrasonically degreased in EnSolv 765 for 2 minutes, immersed into the above aqueous dip for 2 minutes at ambient temperatures and then rinsed under running

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tap water It was noted the water was immediately repelled from the polished surface, which left the samples dry. Samples were tarnish tested as described in Example 1 and all showed enhanced tarnish resistance.

5

**Example 4****Aqueous dip application 2 (detergent degreased samples)**

10 Samples of Argentium Sterling were degreased in a 2% aqueous solution of a detergent (Fairy Liquid) and were then immersed in the treatment solution of Example 3. It was noted that the treated samples had become water-repellent as described in Example 3. Samples were tarnish tested as described in Example 1 and all showed enhanced tarnish resistance. The above test was repeated except that the Fairy liquid in the treatment solution was replaced by a liquid hand soap  
15 (40 ml). When exposed to ammonium polysulphide solution, the samples did not show enhanced tarnish resistance. It is possible that this may have been because the hand soap was more dilute.

**Example 5**

20

**Simultaneous degreasing and anti-tarnish treatment**

The following solutions were prepared:-

- 25
- 1 gram stearyl mercaptan
  - 5 ml EnSolv 765
  - 20ml detergent (Fairy Liquid)
  - 100ml de-ionised water
- 30
- 1 gram stearyl mercaptan
  - 5 ml EnSolv 765

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- 30ml detergent (Fairy Liquid)
- 100ml de-ionised water
- 1 gram stearyl mercaptan (Preferred quantities)
- 5 - 5 ml EnSolv 765
- 40ml detergent (Fairy Liquid)
- 100ml de-ionised water
- 1 gram stearyl mercaptan
- 10 - 5 ml EnSolv 765
- 40ml detergent (Fairy Liquid)
- 500ml de-ionised water
- 1 gram stearyl mercaptan
- 15 - 5 ml EnSolv 765
- 40ml detergent (Fairy Liquid)
- 1000ml de-ionised water.

The solutions were heated to 50°C in an ultrasonic cleaning tank.

20 Samples of polished Argentium Silver were ultrasonically degreased in the solutions for 2 minutes and were rinsed under running tap water. For the first three of the above treatment solutions, it was observed that water was repelled off of the surface leaving the samples dry. Samples treated with the first three solutions above were tarnish tested as described in Example 1 and all showed

25 enhanced tarnish resistance. However, in the case of the samples treated with the last two solutions, water was not repelled off of the surface during the rinsing stage. When the samples dried they showed streaks on the surface which discoloured during the tarnish test. The sample treated with the 500ml solution showed less discolouration than the sample treated with the 1000ml solution. The

30 above experiments show that Argentium silver can be simultaneously degreased and protected against tarnish using a thiol treatment agent applied in an aqueous

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system, and that the more concentrated the stearyl mercaptan/EnSolv/detergent/Water solution, the better the tarnish resistance produced.

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#### Example 6

**Direct Application - Neat Detergent Solutions (solvent degreased/ aqueous degreased samples)**

10 The following solutions were prepared:

- 1 gram stearyl mercaptan
- 5 ml EnSolv 765
- 40ml detergent (Fairy Liquid) (Preferred quantities)

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- 1 gram stearyl mercaptan
- 5 ml EnSolv 765
- 40ml soap (liquid hand soap)

20

The stearyl mercaptan was initially dissolved into the EnSolv. The detergent was then mixed into the solutions. Samples of Argonium Silver were polished and ultrasonically degreased in EnSolv 765 for 2 minutes. The stearyl mercaptan/EnSolv/detergent solutions were then directly applied to the surface of the Argonium samples using damp cotton wool and massaged into lather. The samples were then rinsed under running tap water. In each case, it was noted that water was repelled off of the polished surface, leaving the samples dry. Samples were tarnish tested as in Example 1 by being exposed to neat ammonium polysulphide solution over a period of 1 hour. They all showed enhanced tarnish resistance. The above direct method for applying the Stearyl Mercaptan was tested on samples degreased in a 2% Fairy Liquid aqueous solution. Enhanced tarnish resistance was again achieved.

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### Example 7

#### Cloth Application (solvent degreased samples)

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Cloths were prepared by soaking clean cotton cloth in the following solutions:and allowing the cloths to dry

- 0.1 gram Stearyl Mercaptan dissolved in 100ml EnSolv
- 10      - 0.5 gram Stearyl Mercaptan dissolved in 100ml EnSolv
- 1.0 gram Stearyl Mercaptan dissolved in 100ml EnSolv (Preferred)

15      Samples of Argentium Silver (which had been polished and ultrasonically degreased in EnSolv 765 for 2 minutes) were wiped with the cloths then buffed with clean cotton wool. Samples were tarnish tested as described in Example 1 by being exposed to ammonium polysulphide solution over a period of 1 hour. All of the samples showed enhanced tarnish resistance.

### Example 8

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#### Hexadecyl and octadecyl mercaptan in Fairy liquid

25      Hexadecyl mercaptan (1g) in the liquid state was mixed with Fairy liquid (surfactant containing anionic and nonionic surface active agents) and with water in the quantities indicated below:

	Reference	Fairy liquid (ml)	Deionised water (ml)
	8.1	40	Nil
	8.2	100	Nil
30	8.3	200	Nil
	8.4	40	100

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8.5

40

200

The ingredients of solution 8.2 appeared to mix well without needing the hexadecyl mercaptan to be dissolved in an organic solvent beforehand. A sample  
5 of Argentium silver was immersed in the resulting solution for 10 minutes and rinsed. The surface of the Argentium sample had become hydrophobic, suggesting the formation of a layer of hexadecyl mercaptan attached to the surface of the Argentium silver. It rinsed well in water without any noticeable deposit being left on the surface after rinsing. A region of the sample was rubbed  
10 with cotton wool soaked in EnSolv 765 and then subjected to tarnish testing with neat ammonium polysulphide over a period of 45 minutes. Excellent tarnish resistance was noted, without significant difference between the region that had been treated with EnSolv 765 and the region that had not been so treated. Similar solutions were prepared from octadecyl mercaptan and Fairy liquid. They were  
15 transparent at first, but of lesser stability with separation of a surface layer of octadecyl mercaptan after some months.

### Example 9

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#### Hexadecyl mercaptan in Simple shower gel

Hexadecyl mercaptan in the liquid state was mixed with Simple shower gel (a clear shower gel from Accentia Health and Beauty Ltd, Birmingham, UK, and believed to contain sodium laureth sulfate and cocamidopropyl betaine as  
25 principal surfactants, together with cocamide DEA and incidental ingredients) and with water in the quantities indicated below:

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Reference	HDM (g)	Simple (ml)	Deionised water (ml)
9.1	1	100	Nil
9.2	1	100	100
9.3	5	100	100
5 9.4	1	200	100

Shortly after mixing, solutions 9.1 and 9.4 were completely transparent viscous gels free from noticeable separation of the hexadecyl mercaptan. Sample 9.2 was also completely transparent but had a water-like consistency and again did not exhibit separation of hexadecyl mercaptan. Sample 9.3 which also had a water-like consistency appeared as a milky emulsion when shaken but exhibited separation of hexadecyl mercaptan at the surface on standing.

In a preliminary experiment, a sample of Argentium silver was immersed in solution 9.1 for 10 minutes and rinsed. The surface of the Argentium sample had become hydrophobic, suggesting the formation of a layer of hexadecyl mercaptan attached to the surface of the Argentium silver. It rinsed well in water without any noticeable deposit being left on the surface after rinsing. When tested with neat ammonium polysulfide, excellent tarnish resistance was noted.

Samples of Argentium silver and conventional Sterling silver were prepared as follows. Each sample was polished with Steelbright polish, followed by rouge, and then ultrasonically degreased for two minutes in a 2 wt% Fairy Liquid solution in water at 54°C. It was then further degreased for 5 minutes in ethanol and immersed at ambient temperatures in the test solution. After removal, part of each sample was rubbed with tissue soaked in EnSolv 765 and then subjected to tarnish testing with neat ammonium polysulphide over a period of 45 minutes. Argentium samples showed excellent tarnish resistance and thiol bonding, especially good results being obtained with solutions 9.1 and 9.4 compared to the higher water content solutions 9.2 and 9.3. Solutions 9.1 and 9.4 appeared to provide some tarnish protection for standard Sterling silver also, but



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the thiol layer could be removed easily as was apparent from the differences between the untreated and the EnSolv 765 treated regions.

### Example 10

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#### Mixtures of cocamidopropyl betaine (CPB) and sodium laureth sulfate (SLS)

The above materials were supplied as a thick pourable aqueous liquid and as a highly concentrated somewhat gelatinous liquid (70% active) by Surfactchem Ltd of Leeds, United Kingdom. Hexadecyl mercaptan (1 ml) in the liquid state was mixed with these materials in the quantities indicated below:

	Reference	SLS (ml)	CPB (ml)	Water (ml)
15	10.1	40	40	100
	10.2	40	20	100
	10.3	30	10	100
	10.4	10	30	50
	10.5	30	10	160

20

For solution 10.1, hexadecyl mercaptan was added to a thick mixture of sodium laureth sulphate and cocamidopropyl betaine after which water was added and the solution was mixed cold. The resulting mixture initially had a thick foamy-white texture which on settling turned into a transparent gel. Solution 10.2 was somewhat similar. Solution 10.3 was watery and was initially slightly transparent with lots of bubbles on top of the solution., and on settling overnight it became transparent. Solution 10.4 was mixed with gentle heating to about 35°C Heat appeared to slightly help with the mixing procedure. After a few minutes of mixing the mixture foamed severely. The mixture was allowed to stand overnight and formed a viscous solution. Solution 10.5 was heated to approximately 35°C whilst mixing. Water was last ingredient to be added. Using heat for mixing

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proved beneficial. The solution appeared very foamy but this settled over a few hours (within 12 hours) to form a transparent solution slightly thicker than water.

Argentium silver samples were prepared by polishing in Steelbright and then rouge, ultrasonically degreasing in a 2% aqueous Fairy Liquid solution further degreasing in acetone, immersion in the test solution at ambient temperatures for 10 minutes, and washing under cold running tap water. A lower region of each sample was rubbed with tissue soaked in EnSolv in an attempt to attempt to remove any thiols, after which the sample was left to stand for 45 minutes and were then exposed to a neat ammonium polysulphide accelerated tarnishing test for 45 minnutes.

All the samples showed extremely good hydrophobic properties during the rinsing process which indicates presence of thiols. Water drops were repelled and there was no need to dry each sample. The samples performed well in the tarnishing test with resistance to tarnishing and little difference between the rubbed and un-rubbed regions. It was concluded that the hexadecyl mecaptan in each sample tested had created a tarnish-protective thiol-bonded layer on the surface of the Argentium silver.

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### CLAIMS

1. A method for treating a finished or semi-finished shaped flatware, hollowware or jewellery article of a silver/germanium alloy that has a silver  
5 content of at least 77 wt % and a germanium content of between 0.4 and 7% the remainder principally being copper so as to reduce or further reduce tarnishing of the article such that a sample of the alloy of which the article is made can be supported close above a 20% solution of ammonium polysulphide for at least 30 minutes while retaining a generally untarnished appearance, said method  
10 comprising  
surface treating said article with an alkanethiol, alkyl thioglycollate, dialkyl sulfide or dialkyl disulfide
2. The method of claim 1, wherein the alkanethiol, alkyl thioglycollate,  
15 dialkyl sulfide or dialkyl disulfide has C<sub>12</sub>-C<sub>24</sub> alkyl groups.
3. The method of claim 1 or 2, wherein the alkanethiol, alkyl thioglycollate, dialkyl sulfide or dialkyl disulfide is in an organic solvent.
- 20 4. The method of claim 3, wherein the solvent containing the alkanethiol, alkyl thioglycollate, dialkyl sulfide or dialkyl disulfide is generally neutral.
5. The method of claim 3 or 4, wherein the alkanethiol, alkyl thioglycollate, dialkyl sulfide or dialkyl disulfide is in a solvent based on n-propyl bromide.  
25
6. The method of claim 3 or 4, wherein the alkanethiol, alkyl thioglycollate, dialkyl sulfide or dialkyl disulfide is in (a) a composition obtainable by dissolving said alkanethiol, alkyl thioglycollate, dialkyl sulfide or dialkyl disulfide in an organic solvent and adding to said solution a relatively concentrated aqueous soap  
30 or detergent, or (b) an aqueous dispersion obtainable by dissolving said alkanethiol, alkyl thioglycollate, dialkyl sulfide or dialkyl disulfide in an organic

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solvent, adding to said solution a relatively concentrated aqueous soap or detergent, and diluting the resulting mixture with water.

7. The method of claim 1 or 2, wherein said alkanethiol, alkyl thioglycollate, dialkyl sulfide or dialkyl disulfide is in a composition obtainable by dissolving said alkanethiol, alkyl thioglycollate, dialkyl sulfide or dialkyl disulfide direct in an aqueous mixture of an anionic surfactant and a neutral, amphoteric or zwitterionic surfactant, said mixture being free from solvents other than water.

8. The method of claim 7, wherein said composition comprises as surfactant a betaine.

9. The method of claim 8, wherein the betaine is cocamidopropyl betaine.

10. The method of any of claims 7-9, further comprising an anionic surfactant.

11. The method of claim 10, wherein the anionic surfactant is of the formula  $RO-(CH_2CH_2)_nSO_3M$  wherein R represents  $C_{10}-C_{18}$  alkyl, n is 2-6 and M represents a monovalent cation.

12. The method of claim 11, wherein the anionic surfactant is a monovalent cation salt of laureth sulfate.

13. The composition of any of claims 7-12, comprising amphoteric or zwitterionic surfactant and anionic surfactant in a weight ratio of from 1:10 to 10:1.

14. The method of claim 9, wherein the aqueous mixture comprises sodium laureth sulfate and cocamidopropyl betaine.

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15. The method of any preceding claim, wherein the alkanethiol or alkylthioglycolate is selected from stearyl mercaptan (octadecyl mercaptan), cetyl mercaptan (hexadecyl mercaptan), stearyl thioglycollate and cetyl thioglycollate.

5 16. The method of any preceding claim, wherein the alloy consists, apart from impurities and grain refiner, of 92.5-98% silver, 0.3-3% germanium, and 1-7.2% copper, by weight of the alloy, together with 1-40 ppm boron as grain refiner.

10 17. The method of claim 16, wherein the ternary alloy consists, apart from impurities and grain refiner, of 92.5-96% silver, 0.5-2% germanium, and 1-7% copper, by weight of the alloy, together with 1-40 ppm boron as grain refiner.

18. The method of any of claims 1-15, wherein the alloy is a quaternary alloy of silver, copper, zinc and germanium.

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19. The method of any preceding claim, comprising the further step of introducing the treated article into packaging.

20 20. The method of claim 19, wherein said packaging includes a presentation box.

21. The method of claim 20, wherein the packaging includes external wrapping for the presentation box.

25 22. Use of a  $C_{12}$ - $C_{24}$  alkanethiol, alkyl thioglycollate, dialkyl sulfide or dialkyl disulfide in the preparation of a tarnish inhibitor for an article of a silver/germanium alloy that has a silver content of at least 77 wt % and a germanium content of between 0.4 and 7%, the remainder principally being copper, so as to reduce tarnishing of the alloy such that a sample can be supported  
30 close above a 20% solution of ammonium polysulphide for at least 30 minutes while retaining a generally untarnished appearance.

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23. A finished or semi-finished shaped flatware, hollowware or jewellery article of an alloy of silver containing an amount of germanium that is effective to reduce firestain and/or tarnishing and that has been treated with a C<sub>12</sub>-C<sub>24</sub> alkanethiol, alkyl thioglycollate, dialkyl sulphide or dialkyl disulphide and that exhibits a tarnish resistance such that a sample of the alloy of which the article is made can be supported close above a 20% solution of ammonium polysulphide for at least 30 minutes while retaining a generally untarnished appearance

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